

REVIEW ARTICLE

A Review on Thermal Energy Storage Using Composite Phase Change Materials

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Abstract: Background: This paper intends to provide the elementary understanding about the development of thermal energy storage systems. Reviews of storage system performance are carried out from various characterization studies, experimental work, numerical investigations and patents. Several techniques employed to enhance the thermal performance have been reviewed and discussed. Composite phase change materials are the best alternative to achieve the cost feasibility in thermal energy storage systems without compromising the storage capacity.

Objective: The purpose of this study is to give an outline and history of the thermal energy storage systems and enlighten the techniques used for storage density enhancement without significant modifications in the design.

Methods: In this study, three methods such as, characterization studies, experimental work, numerical investigations and patents. It also addresses many research articles and recent patents on the thermal storage systems, various techniques adopted and applications of such systems.

Results: Composite phase change materials are the best alternative to achieve the cost feasibility in thermal energy storage systems without compromising the storage capacity. Carbon based nanoparticles show excellent properties in the composite phase change materials.

Conclusion: Composite phase change materials have greater potential for thermal energy storage applications and especially carbon-based nanoparticles like graphene, graphene oxide, carbon nanotubes, fullerene, graphite, graphite oxide, extracted graphite etc., are greatly enhancing the thermo-physical properties of composite phase change materials. Combination of paraffin-based phase change materials and carbon-based nanoparticles can be used for the future thermal energy storage applications.

Keywords: Composite phase change materials, copper nanoparticles, fullerene, graphene, graphene fibers, heat transfer enhancement, nanoparticles, paraffins, thermal conductivity, thermal energy storage.

1. INTRODUCTION

In recent years, major efforts have been put forward for effective harnessing in various forms of energies. Continuous increase in the level of greenhouse gas emissions and the hike in fuel prices are the driving forces to look towards reutilization of Thermal Energy Storage (TES) [1]. To attain the complete proficiency various new technologies are adopted to tap energy from uncovered areas and progressed to a higher level [2]. Several techniques are implemented for specific required applications which are discussed in subsequent chapter. Reutilization of low-grade energy available between ambient temperature and 200°C is not favorable due to technical and economical constraints to acquire exergy and energy from low grade heat. Large amount of heat

energy is available between 35°C and 55°C from various process industries [3]. It is known that thermal energy can be stored in three different forms such as, sensible heat, latent heat and thermochemical by changing its internal energy. Sensible heat storage causes change in temperature whereas latent heat is stored during phase transition. Latent heat storage is an effective way due to its high energy storage density at constant temperature. The most basic requirement for storing the latent heat is Phase Change Material (PCM). The PCMs are of various categories and their selection depends on the working temperature range like low-temperature thermal storage (melt range is between 0°C and 120°C) used for several applications such as, domestic water heating, direct heating or heat-pump assisted space heating, greenhouse heating, solar cooling, etc. Medium temperature thermal storage (100 to 180°C) used for many industrial processes, e.g. food, paper, chemical industries etc. High-temperature thermal storage (up to 900°C) used for power plant and metallurgical applications [4]. Storage of energy

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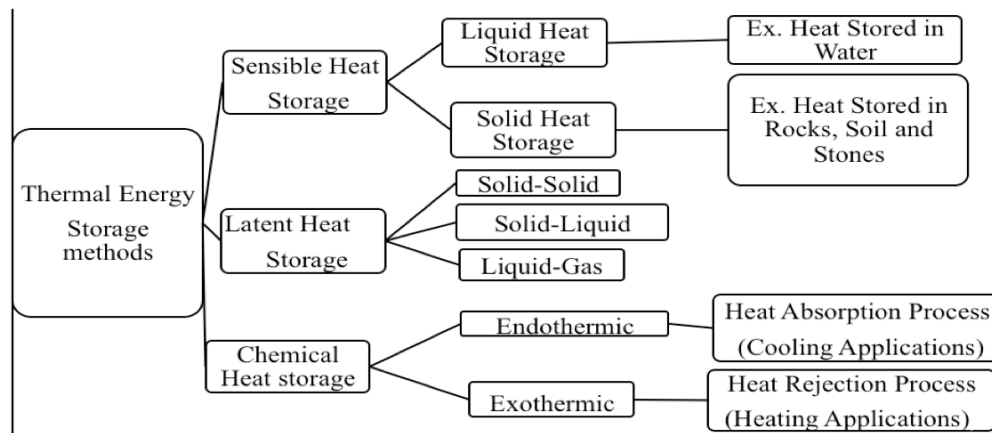


Fig. (1). Different methods of thermal storage.

eliminates or minimizes the gap between energy supply & demand and also improves the performances of energy storage systems. The PCMs become significant for its excessive energy storage capacity, it reduces the fluctuation of temperature during the day period and stabilizes temperatures in the required range. Researchers have shown much interest towards encapsulation of PCMs for large scale applications. PCMs with limited storage capacity can be blended with any suitable nanoparticles to overcome the limitations of composite Phase Change Materials (CPCMs) [5].

1.1. Thermal Energy Storage Techniques

There are different methods of thermal energy storage which are shown in Fig. (1). It is seen that, the storage method depends on the availability of the energy formation and required applications. First is latent heat storage where large amount of heat energy is stored during phase change process. The phase change may be solid-solid, solid-liquid and liquid-gas. In solid-solid PCMs, only molecular crystalline structure changes and its volume requirement limits its storage capacity. Solid-gas or liquid-gas phase change materials exhibit higher latent heat of fusion, but these are not preferred due to their large volume requirement after phase transition. Therefore, solid-liquid phase change materials are considered to be most practical and economical [6]. The alternate approach for sensible heat storage is latent heat storage. Previous studies have shown that, latent heat storage provides low cost storage systems by using easily available PCMs [7].

2. CLASSIFICATION OF PHASE CHANGE MATERIALS

Phase change materials are materials which melt and solidify at a certain temperature when it is heated or cooled subsequently and the temperature at which phase change occurs is called as the phase change temperature of that particular material. The selection of proper candidate PCM for particular application is essential, for different range of applications so that proper material can be selected accordingly. Commonly available PCMs are classified as shown in Fig. (2) [8] and [9]. It is quite unfortunate that no single material can fully satisfy all the desirable properties required for thermal storage applications. Apart from the disadvantages related to volume requirements, the organic PCMs work as essential heat storage materials.

Paraffins are the substances which have straight chains of hydrocarbons with a small amount of branching near the end of the chain, which are characterized as alkanes (C_nH_{2n+2}). These are again classified depending upon the chain length of the alkane. Paraffins with hydrocarbon of branched-chain structures are called iso-paraffins. The inorganic PCMs are not preferred in the TES systems due to their supercooling effect, toxicity, corrosivity and other harmful properties. However, usage of paraffin is also complicated due to their undesirable leakage problem in molten state [10]. To achieve better storability with safety, two or three PCMs are mixed to form binary or ternary eutectics [11]. Eutectic is a composition of two or more materials, each of which melts and solidifies without forming accumulation separately and changes phase without segregation of component materials, e.g. salt hydrates (eutectic mixture) have high storage density and higher thermal conductivity as compared to paraffins.

2.1. Characteristics of Phase Change Materials

Table 1 shows the phase change materials and their properties [12]. The PCMs selected for particular application should possess the following characteristics.

- Should sustain the operating temperature with proper phase transition
- Should possess high latent heat to reduce the size of the storage structure
- Should possess high thermal conductivity to make system charge faster
- Should possess high density to provide better stability during melting and solidification
- The volume required for phase transition must be small and it should not require supercooling.
- Should be chemically stable (i.e. should not degrade and should be non-toxic and non-explosive).

3. ROLE OF COMPOSITE PHASE CHANGE MATERIALS

Storing thermal energy using Composite Phase Change Materials (CPCM) is one of the alternatives to enhance the thermo-physical properties of PCMs, which are delivering appreciable and interesting results with different composi-

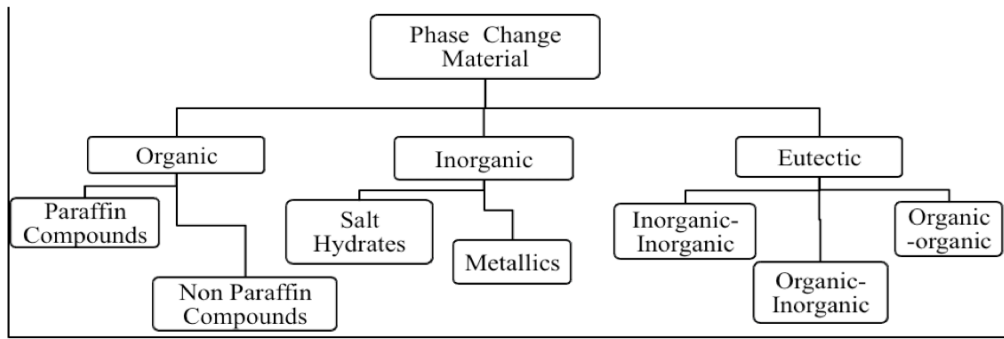


Fig. (2). Classification of PCMs.

Table 1. Phase Change Materials and Their Properties [12].

Material	Type	Desirable Properties	Undesirable Properties	
Organic Materials	Paraffins	Non-corrosive	Low thermal conductivity	
		Chemically stable up to 500°C	Non-compatible with the plastic container	
		Less expensive	Moderately flammable	
		Reliable		
	Non Paraffins	Safe and predictable	Inflammability	
		High heat of fusion		Low thermal conductivity
		No supercooling		Low flashpoints
	Some fatty acids can be used for low-temperature latent heat thermal energy storage applications	Instability at high temperatures		
Inorganic Materials	Salt Hydrate	High latent heat of fusion per unit volume	Slightly toxic	
		Relatively high thermal conductivity (almost double of the paraffins)	Requires supercooling	
		Change in volume is small while melting		
		Non-corrosive		
		Compatible with plastics		
	Metallic	High thermal conductivity	Low specific heat	
		Low heat of fusion per unit weight	Relatively low vapor pressure	
		High heat of fusion per unit volume		

tions of various base materials and additives. Materials with high energy storage capacity used for thermo-chemical heat storage are selected with respect to the suitable range of chemical reaction temperatures [13]. Recently, researchers adopted encapsulation method to enhance the performance of TES by mixing of nanomaterials with PCMs. This is to advance certain properties such as low thermal conductivity, supercooling and incongruent melting (solid substance does not melt uniformly, decomposing into another solid and a liquid with different compositions) [14].

Metals and metal oxides can be added to traditional PCMs in which carbon-based nanomaterials are more suitable because of their excellent thermo-physical and thermo-chemical properties. For lower temperature range inorganic PCMs are suitable but lead to corrosion, incongruent melting

and supercooling. To overcome these confines one can go for organic PCMs, but organic PCMs have relatively lower thermal conductivity and heat transfer rate, which can be eliminated by adding metals and metal oxides.

3.1. Thermal Properties Enhancement Using Characterizations of Composite Phase Change Materials

Ceramic composites are used in Thermal Energy Storage (TES) devices with significant enhancement of thermo-physical properties. Several experiments are conducted to investigate the ceramic behaviour with different material compositions, in ceramics a highly conductivity additive material is mixed to provide good structural stability to the PCM [15]. The high thermal conductivity material increases the overall thermal conductivity of the composite material,

such as magnesium oxide as the skeleton to provide structural stability. It is well known that, carbon allotropes are thermal conductivity enhancing materials with good physical and chemical stability [16]. Eutectic salt of lithium and sodium carbonate can be used as PCM for medium and high temperature TES applications. To provide wettability and stability the composite structure it can be blended with carbon allotropes [17].

A polyurethane based PCM synthesized by polymerization method in which poly (ethylene glycol) (PEG) is modified with graphite nanoplatelets and it is characterized by Fourier-Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), Scanning Electron Microscope (SEM) and ultrasonic techniques. It provides better crystal structure and enhanced thermal conductivity with increase in graphite nanoplatelets concentration [18]. In PEG and Boron Nitride (BN), CPCM Graphene Nanoplatelets (GNP) are introduced, presence of GNP enhanced thermal conductivity and thermal energy conversion [19].

Polymorphic nature of mannitol is suitable for thermal storage application for providing thermal stability. To find the thermo-physical behaviour of mannitol, a galactitol and mannitol mixture is prepared and analyzed with the help of DSC, X-Ray Diffraction (XRD) analysis and FTIR. The eutectic mixture at 30:70 molar fraction of galactitol and mannitol ($\Delta H_{fus} = 292\text{J/g}$) at melting point 153°C provided better cyclic, thermal and chemical stability in comparison with individual state in nitrogen or air with suppressed supercooling [20].

Polyethylene Glycol (PEG) is a white free flowing powder or creamy white flakes which have been considered as a promising PCM for TES applications due to its relatively high latent heat of fusion, congruent melting, freezing behavior, appropriate melting temperature range, non-corrosiveness and non-toxicity [21]. A CPCM of PEG and cellulose / Graphene Nanoplatelets (GNP's) aerogel with 5.3wt.% of GNP in CPCM enhanced the thermal conductivity up to 463% and also provided better shape stability by developing porous cellulose network which prominently influenced the thermal conductivity [22]. Polyurethane polyethylene glycol (PUPEG) is modified with graphene (as a chain extender) to enhance the thermal conductivity and thermal stability. The increase in graphene concentration, increases the thermal conductivity and CPCM retained its thermal reliability even after 100 thermal cycles both under air and nitrogen atmosphere [23]. In order to achieve better thermal stability even after large number of thermal cycles, a eutectic mixture of Myristic Acid/Palmitic Acid/Sodium Laurate (MA/PA/SL) is analyzed. The CPCM sustained up to 1000 thermal working cycles with same charging / discharging ability with minor changes in the conversion capability [24]. Eutectic mixture of sodium nitrate and potassium nitrate with alumina nanoparticles greatly influences the specific heat capacity. The nanoparticle concentration increases specific heat capacity upto (30.6%) at 0.78% mass fraction [25].

The PCMs blended with nanoparticles like expanded graphite, exfoliated graphite nanoplatelets or carbon nanotubes (CNTs) improves thermal properties but structural sta-

bility is unaltered. To provide better structural stability microcrystalline cellulose and light-weight cellulose are the possibilities, which forms three-dimensional strong porous structures. While considering about most reliable material for TES application paraffins and paraffin based CPCM are most beneficial, but the drawback is lower thermal conductivity, because of which charging / discharging time obligation is more. To reduce the charging / discharging time nanofillers are used, primarily carbon based nanomaterials, such as short and long multi-walled carbon nanotubes (S-MWCNT's and L-MWCNT's) carbon nanofibers and graphene nanoplatelets. Among these, only S-MWCNT's exhibited the best dispersion due to its smaller geometry. GNPs shown highest thermal conductivity enhancement in composite material nearly 170% at 5wt% of loading, only few layers of thin graphene are not favorable to enhance thermal conductivity due to greater thermal interface resistance [26].

Experimental and numerical investigation of paraffin and copper foam based CPCM exhibited enhanced TES capacity for shorter duration of thermal storage [27]. Paraffin with nano zinc oxide in tubular shape shows satisfactory results for thermo-physical properties enhancement but specific heat capacity is reduced (7%) [28]. Usage of pure metals does not give appreciable results, to look forward for better performance metal oxide and metal hydrates are also used. Among many transition metal oxides, RuO_2 is preferred for electronic supercapacitor devices due to its advantages like higher reversible redox reactions, long life cycle and metallic type conductivity. These excellent properties of RuO_2 motivated researchers for thermal storage applications [29]. Ruthenium (*Ru*) and Iridium (*Ir*) nano-oxide properties are altered by changing oxide compositions, addition of Iridium eliminates the catalyst passivation and improves the activity at higher potential [30]. To improve the existing potential, preferably the thermo-chemical systems working under $400\text{-}1200^\circ\text{C}$ range (for the thermo-chemical storage applications) metal carbonates, hydroxides and metal oxides provides significant results.

The CPCM prepared and characterized using superoleophilic graphene nickel foam as porous supporting material, SEM, XRD images indicated crystal structure arrangements and thermal properties are measured using DSC. This micro-structural analysis revealed that the excellent thermal conductivity and thermal stability of CPCM. A form-stable Expanded Graphite (EG) / Stearic Acid (SA) CPCM has better thermal stability for wide operating temperature range with excellent thermal performance. Form-stable EG/SA CPCM reduced porosity and considerably improved the TES capacity per volume. But addition of Expanded Graphite (EG) has insignificant impact on phase change temperature of CPCM.

Palmitic Acid (PA)/ SA and Graphene nano Platelets (GnPs) and EG of various proportions are fabricated and analyzed for thermo-physical properties. This causes improvement of thermal storage and faster release rate [31]. CPCM of Graphene Aerogel (GA) and Octadecanoic Acid (OA) have thermal conductivity (14 times) more than that of the base material at 20vol% loading and with higher TES capacity [32]. Graphite nanofibers mixed with paraffin is studied with different parameter variations like aspect ratio,

power density, solidification and melting time. The results shown reduction in melting and solidification time by 61% and enhancement of thermal storage capacity (up to 48%) [33].

The betterment of CPCM for medium and high-temperature thermal storage applications salt based composite materials are prepared and investigated. The thermal characteristics shown greater chemical stability and higher thermal conductivity by addition of magnesium oxide and carbon allotropes. The oxides of lithium carbonate increased dispersion in amorphous powder which increases the specific heat capacity of molten salt. These molten salt nanofluids shown greater potential towards concentrated solar power systems [34]. Addition of 0.05wt% of graphene in epoxy/graphene composite enhanced the thermo-mechanical properties and better dispersion in composite. Higher concentration of graphene causes reduction in mechanical properties due to aggregation of graphene particles [35]. Aluminate cement and nano magnesium oxide CPCM considerably affects both mechanical and thermal properties. But optimizes the pore distribution and hence thermal conductivity enhanced by 34.8% and 40.8% at 1wt% and 2wt% respectively, overall characterization studies representing the similar facts, to achieve better TES capacity the CPCMs are greater potential materials [36].

Paraffin usage is complicated due to their leakage problem during the melting process, this drawback confines paraffins for thermal storage application. To compensate this problem Rude-Palygorskite (Pal) is mixed with the paraffin and the composite is analyzed through FTIR and DSC. The composite shown improves thermal properties and better stability even after 500 thermal cycles with negligible change (5J/g) in latent heat capacity. Investigation is also carried out [37] to avoid the leakage by mixing PEG (upto 85 wt%) in the composite, analysis shown better thermal reliability and stability.

Light density, high thermal conductivity, heat storage capacity and good stability making PEG attracting PCM [38]. In order to improve the thermal properties Myristyl Alcohol (MA) is blended with nickel and copper metal foams. Thermal conductivity enhancement is 88% with reduced specific heat capacity by 29% [39]. The leakage problems of PEG diverted attention towards the supporting matrix to stabilize its internal structure. Hydroxyapatite (HAP) is one of the attempts to improve its stability for thermal energy storage application [40]. The chemical compatibility of the individual materials is significant like diatomite and sodium nitrate, used as PCM with combination of graphite particles. The composite shown better chemical compatibility and thermal conductivity increased due to graphite incorporation [41]. TES systems based on gypsum composites also significantly reformed thermal performance with increase in diatomite/paraffin content [42].

Continuous efforts making thermal storage systems more effective through different techniques like encapsulation, micro encapsulations etc., poly (methyl methacrylate-co-methacrylic acid) (PMMA-MAA) is prepared from Methyl Methacrylate (MMA) and Methacrylic Acid (MAA) used for encapsulation. The thermal conductivity is relatively im-

proved and slightly higher storage capacity is achieved [43]. A composite of $\text{LiNO}_3\text{-KCl-NaNO}_3$ / expanded graphite shown higher thermal conductivity and hence much faster charging rate is achieved than the base material [44]. Lauric Acid (LA) impregnated into modified sepiolite (SEP) and the composite shown better thermal reliability even after 200 thermal cycles [45]. To reduce the cost of energy conservation using of easily available materials will be the efficient way such as waste recyclable plastics, polyethylene etc. High Density Polyethylene (HDPE) and Stearyl Alcohol (SAL) blended Expanded Graphite (EG) exhibited improvement in the thermal conductivity [46].

3.2. Numerical Studies of Composite Phase Change Materials

The governing equations [47] used for numerical simulations are as follows:

Continuity equation:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{U}) = 0 \quad (1)$$

Momentum equation:

$$\frac{\partial}{\partial t} (\rho \vec{U}) + \nabla \cdot (\rho \vec{U} \vec{U}) = -\nabla P + \rho \vec{g} + \nabla \cdot \bar{\bar{\tau}} + \vec{F} \quad (2)$$

Where P is the static pressure, $\bar{\bar{\tau}}$ is the stress tensor, and $\rho \vec{g}$ and \vec{F} are the gravitational body force and external body forces, respectively.

Energy equation:

$$\frac{\partial(\rho H)}{\partial t} + \nabla \cdot (\rho \vec{U} H) = \nabla \cdot (K \nabla T) + S \quad (3)$$

Where H is the enthalpy of the CPCM, T is the temperature, ρ is density of the CPCM, K is the thermal conductivity of CPCM, \vec{U} is the velocity and S is volumetric heat source term.

Paraffin with copper nanoparticles (1wt%) improved thermal conductivity and reduced melting time up to 13.1% [48], enclosure geometry and heating face also plays a significant role in reducing the melting/solidification time [49]. Various forms of CPCMs are developed such as, slurries, eutectics and different material blends to improve the heat transfer rate. Slurry is a binary composition of carrier material, water (continuous phase) and PCM (dispersed phase), are called phase change slurries. Phase change slurries uses the latent heat capacity of the PCM and sensible heat capacity of the carrier material in order to store or transfer thermal energy [50]. A phase change slurry (10wt% paraffin) is employed to analyse its TES capability. It is seen that the energy stored in the slurry was 75% more than the energy stored in water at a same temperature and convective heat transfer coefficients also increased up to 25% [51].

An attempt is made to study the thermo-physical properties in micro scale, Molecular Dynamics (MDs) approach is employed to analyse the thermo-physical properties of crystalline octadecane and octadecane-water slurry [52]. The numerical results exhibited that there was reduction in heat capacity of octadecane slurry with increase in octadecane mass fraction [53]. n-Octadecane with copper oxide (CuO) nanoparticle suspensions are studied for development of

melting interface and melt volume fraction under constant heat flux conditions. Results shown that, the thermo-physical properties are amplified with increase in nanoparticle concentration up to a specific percentage. Above the critical limit, there is adverse effect due to increase of viscosity, agglomeration and precipitation [54].

Nanoparticle enhanced Phase Change Material (NePCM) was investigated numerically to analyze the copper nanoparticles sizes (diameter of 2 and 5nm) suspended in water, as the particle size is reduced, the interface morphology changed from uniform to nonuniform dendritic structure during solidification process. By reducing the size of the nanoparticles, solidification time was reduced due to improvement of thermal conductivity [55]. A mixture of water and copper nanoparticles possesses high heat release rate compared to the conventional PCMs and its higher thermal conductivity makes it promising material for TES applications [56]. Another effort was made to reduce the melting and solidification time of PCM (paraffin) by mixing alumina nanoparticles and perceived the time saving of 8% to 20% by adding only 3 to 8% by volume. Alumina nanoparticles activate PCM to perform better which results in faster solidification [57].

To improve the heat transfer rate, spherical encapsulation arrangement is made in a thermal storage tank using CPCM (mixture of 0.4% copper nanoparticles and 99.6% of erythritol). The thermostatic oil bath and CPCM sealed in the balls. The numerical study results shown the influence on heat dissipation rate through phase change ball and the interface are moved during heat release process [58]. To understand the solidification and melting process for CPCM which is encapsulated inside cylindrical enclosures, the transient interface positions are located and complete phase change time was predicted by using two models for solidification and three models for melting. The heat generation delays the solidification and accelerates the melting process.

Bechiri *et al.*, [59] proposed the numerical model for melting and solidification of NEPCM. It was found that the heat generation increases at the time of phase change process because of increase in thermal conductivity of PCM. Addition of nanoparticles decreased the phase change process which leads to the acceleration of heat diffusion within NePCM. To analyze the TES capacity and discharge efficiency a numerical transport model of porous media and phase change model of thermocline bed was developed. The packed bed shown enhancement in the energy storage capacity, heat rejection efficiency and discharging time with increase in CPCM concentration [60].

The numerical investigation was carried out for thermal stability, supercooling, corrosion test and reliability of inorganic hydrated salt $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ with copper as nanoadditives [61]. The computed results shown good thermochemical stability even after 300 thermal charging /discharging cycles. This CPCM enhanced the latent heat per unit volume, but the only drawback was lower thermal conductivity. Enthalpy of fusion and heat storing capacity in both solid and liquid phases of LiNO_3 , NaNO_3 , and KNO_3 is prominently better [62]. Out of these, sodium nitrate (NaNO_3) metal matrix possessed higher thermal conductivity,

good mechanical properties and larger surface area. The heat transfer co-efficient of CPCM was enhanced up to 28.1 times and heat conduction, as well as both melting and solidification time duration was reduced, along with this the porosity of the copper matrix enhanced the conductivity of composite [63]. Heat transfer enhancement and energy storage performance of CPCM can be achieved with CuO nanoparticles, by adding 0-4vol% of CuO nanoparticles in HTF and 0-7vol% of CuO nanoparticles with PCM [64].

Energy storage technology balancing mismatch between energy supply and demand during day and night. The air conditioning system combined with ice storage can use during night for reducing operating costs. The commercial evaluation shown that CPCM usage is profitable with a short payback period [65]. The overall heat transfer rate is increased but the convective heat transfer coefficient is suppressed for a higher concentration of nanoparticles due to increase in viscosity. Detail summary of various numerical investigation is given in Table 2 to compare the different parameters.

4. EXPERIMENTAL INVESTIGATIONS OF THERMAL ENERGY STORAGE USING COMPOSITE PHASE CHANGE MATERIALS

Two methods of thermal storage are introduced as Cascade Latent Heat Storage (CLHS) and Non-Cascade Latent Heat Storage (NLHS) [66]. The CLHS utilizes the phase change process more effectively compared to NLHS at uniform outlet temperature and using less quantity of salt, CLHS achieves the greater storage capacity. To enhance the thermal conductivity of CPCM, metallic foam and metallic sponge are mixed and employed for various cooling rates under unsteady conditions. The inserts enhanced thermal conductivity of CPCM [67]. Erythritol is also a potential material for TES application but the thermal conductivity is relatively lower. To overcome this, Expanded Graphite (EG) was added by using direct contact synthesis method. The performance is evaluated and found enhanced thermal conductivity of the composite with adverse effect on latent heat capacity. Addition of 4wt% of EG enhanced thermal conductivity by 2.5 times and specific heat capacity is reduced by 2.59%. The investigation also reveals reduction of 16.7% melting time but solidification time remain same [68].

Compared to salt hydrates, the organic PCMs have lower volumetric TES capacity. Several experiments are carried out to investigate such as paraffin wax embedded with aluminum powder. The results shown 60% reduction in charging time after addition of aluminum powder [69]. For enhancing thermal storage density of paraffin (n-docosane) EG is the suitable candidate material to obtain form-stable CPCM. Influence of EG is studied for thermal conductivity enhancement using transient hot-wire method. Latent Heat Thermal Energy Storage (LHTES) characteristics of paraffin like, melting time, melting temperature and latent heat capacity was investigated with the help of DSC. It is found that the paraffin/EG CPCM with the mass fraction of 10% EG shown the most favorable results [70].

Single and multi-walled carbon nanotubes, carbon blacks, exfoliated graphite nanoplatelets with comparatively higher conductivities are used to prepare CPCM which be-

Table 2. Numerical Models Studied for TES Applications by the Various Researchers.

Authors	Dimensionality	Geometry	Steady/Transient	Parameters Studied
(Wang and Ling 2016) [40]	MD	NA	Steady	Molecular dynamics
(Rao <i>et al.</i> 2012) [52]	MD	NA	Transient	Melting behavior
(Cascetta <i>et al.</i> 2014) [54]	One	NA	Transient	Charging, discharging and thermal profile
(Parsazadeh and Duan 2017) [64]	Two	Cylindrical	Transient	Role of nanoparticles in the HTF and their effects on the melting rate
(Mahdi and Nsofor 2016) [57]	Two	Cylindrical	Transient	Flow behavior and heat transfer characteristics during solidification of a nano-PCM
(Lv <i>et al.</i> 2016) [61]	Two	Cylindrical	Transient	Melting and solidification process
(Lu <i>et al.</i> 2014) [60]	Two	Square	Transient	Energy storage density
(Lu <i>et al.</i> 2014) [60]	Two	Cylindrical	Transient	Energy storage performances
(Wu <i>et al.</i> 2012) [48]	Two	Square	Transient	Melting of the PCM
(Delgado <i>et al.</i> 2012) [51]	Two	Circular	Transient	Influence of fluid temperature on wall temperature
(Khodadadi and Hosseinizadeh 2007) [56]	Two	Square	Transient	Solidification process of a water/copper nanoparticles
(Zhang <i>et al.</i> 2016) [58]	Three	Spherical	Transient	Charging, discharging and thermal profile
(Bechiri and Mansouri 2016) [59]	Three	Cylindrical	Transient	Melting and solidification process
(Li and Wu 2014) [51]	Three	Cube	Transient	Phase distribution during melting process
(El-Hasadi 2013) [55]	Three	Square	Transient	Solidification process of a water/copper nanoparticles
(Youssef <i>et al.</i> 2013) [50]	NA	NA	NA (Not available)	Melting and solidification

come electrically and thermally more conductive at much lower loading levels. The results influences in-depth study of different types of exfoliated graphite nanoplatelets (xGnP-1 and xGnP-15) in paraffin wax which provides improved thermal conductivity and stability to CPCM with large aspect ratio, low interface density and better orientation in presence of xGnP nanoplatelets [71].

Two different paraffins namely, docosane and hexacosane with melting temperature 317.15 and 329.45K are Investigation for TES application [72]. Sulfonated has carried out at three different mole percentage for increasing the LHTES capacity and found that the samples prepared are absorbing and dissipating more energy than the pure paraffin. Sulfonated docosane and hexacosane effect is insignificant on freezing and melting points. It is clear that sulfonation method is suitable for enhancing LHTES capacity of paraffins. Experimental investigation of the TES capacity and discharging efficiency of d-mannitol and hydroquinone. The working fluid used was thermal oil with working temperature 373 to 673K [73]. For same operating conditions, TES of d-mannitol is greater than that of hydroquinone. The enhancement was seen up to 30% and 20% during charging and discharging process respectively and improvement in the latent heat is 10% and 16% respectively. Little modification is done in design by providing fins on the rectangular enclosure of PCM reduces the melting time and hence increases total heat transfer rate with increasing number of fins. On the other hand, the inverse effect is seen while wall temperature is raised [74]. Paraffin wax contains a straight chain of hydrocarbons (> 75%) and very small amount of branching.

Commercially available waxes may range about 8-15 carbon-number with a volume shrinkage less than 12% during freezing [75]. Beeswax of the honey bee is a complex mixture of long-chain alkanes, alkenes, monoesters, diesters, hydroxy-monoesters and fatty acids which can be utilized for similar applications [76]. The Thermal Storage Unit (TSU) was modeled with bee wax and copper helical coils are inserted into it for flowing heat transfer fluid. Series of charging/discharging cycles have been carried out, the results shown that bee wax is the best naturally available PCM, which can be used for low-temperature TES applications [77]. The effects of nano-additives on thermo-physical properties of PCM's are listed in Table 3.

4.1. Recent Patents on Thermal Energy Storage Systems

A thermal energy storage container which includes a U-shaped outer shell in which attachment element is inserted and surrounded by lid. The lid attachment element used to engage a complementary container attachment element [78]. A TES container is implemented which consists a shell compartment used to store TES material with modifications [78] as extension of the same work TES model is developed with reversed bell-shaped container inside of which TES material is to be filled to store the thermal energy [78]. The scope of the implementation is translucent or transparent panels, where both the panels can separate without affecting the performance [78], further improvement in the TES is usage of porous material, the TES porous material is filled at the top portion of the container which transfers the heat from top

Table 3. Effect of Nano-Additives on Thermo-Physical Properties of PCM's with Different Combinations.

Authors	CPCM Combination		Parameter Studied	Effects
	Base PCM	Additives		
(Ge et al. 2014) [16]	Eutectic salt of lithium carbonates (43%) and Sodium carbonates (57%) (LiNaCO ₃)	MgO, Natural graphite flakes and Carbon Nanotubes (CNTs)*	Thermal conductivity (K) and Thermal Storage Density (TSD)	$K = 4.3$ (W/m.K), TSD = 530kJ/kg
(Ye et al. 2014) [17]	Na ₂ CO ₃ /MgO	Multi-Walled Carbon Nanotubes (MWCNTs)*	Thermal energy storage, chemical compatibility and thermal stability	Improved*
(Pielichowska et al. 2016) [18]	Polyurethane	Graphene*	Thermal reliability and chemical stability	Improved*
(Paul et al. 2015) [20]	Eutectic mixture of galactitol (30%) and mannitol (70%)	Graphite powder and Silver Iodide (0.5wt%)	Temperature and enthalpy of crystallization	Improved up to 34%
(Torkkeli 2003) [21]	Polyethylene glycol (PEG)	Acrylic Polymers*	K and TSD	Improved*
(Yang et al. 2016) [22]	Polyethylene glycol (PEG)	Microcrystalline cellulose and GNPs (5.3wt %)	K, Shape stability and latent heat of fusion	K enhanced by 463% with good shape stability and Large latent heat of fusion
(Fauzi et al. 2014) [24]	Myristic Acid (MA)	Palmitic Acid (PA) and Sodium Laurate (SL)*	Thermal properties, chemical stability and thermal performance	Improved*
(Schuller and Lalk 2015) [25]	Sodium nitrate and potassium nitrate (60:40 mole fraction)	Alumina nanoparticle (0.78%)	Specific heat	Specific heat enhanced up to 30.6%
(Fan et al. 2013) [26]	Paraffin wax	CNTs (S-MWCNTs), long MWCNTs (L-MWCNTs), CNFs, and GNPs (5wt. %.)	K	K enhanced up to 164%
(Yuan et al. 2016) [31]	Palmitic-Stearic Acid (PA-SA)	Graphene nanoplatelets (GnPs) (nano scale) and EG (micro- scale) *	K	K of the CPCM enhanced 2.7 times with GnPs and 15.8 times with EG
(Zhong et al. 2013) [32]	Octadecanoic Acid (OA)	Graphene Aerogel (GA)*	K	K enhanced 14 times
(Sanusi et al. 2011) [33]	n-Tricosane	Graphite nanofibers (GNFs)*	Melting time and solidification time	GNF shorten solidification time by 61%
(Saha and Pal 2016) [35]	Epoxy	Graphene oxide and graphene*	Thermal and mechanical properties	Improved*
(Yuan et al. 2014) [36]	Aluminate cement paste	Nano-MgO (NM) and Polycarboxylate*	K	K enhanced up to 40.8%
(Shuying et al. 2012) [48]	Paraffin	Copper nanoparticles (1wt%)	Melting characteristics	Melting time reduced by 13.1%
(Youssef et al. 2013) [50]	Clathrate hydrates	Water*	Thermal characteristic	Improved*

Table (3) contd....

Authors	CPCM Combination		Parameter Studied	Effects
	Base PCM	Additives		
(Delgado <i>et al.</i> 2012) [51]	Paraffin	Water*	Heat transfer phenomenon	Heat Release Rate (HRR) enhanced by 25%
(Wang <i>et al.</i> 2016) [53]	Water	Octadecane*	TSD	Heat Capacity (C_p) reduced with increase in octadecane mass fraction*
(El-Hasadi 2013) [55]	Water	Copper nanoparticles*	Melting and solidification characteristics	Shorten the melting time*
(Mahdi and Nsofor 2016) [57]	Paraffin	Alumina nanoparticles (3-8%)	Melting characteristics	Melting time shortens 8% and 20% for 3 and 8% of nanoparticles respectively
(Lv <i>et al.</i> 2016) [61]	Hydrated salt $Ba(OH)_2 \cdot 8H_2O$	Copper nanoparticles*	Heat transfer rate	Heat transfer efficiency improved*
(Li and Wu 2014) [63]	Sodium nitrate ($NaNO_3$)	Porous copper matrix*	Heat transfer characteristics	K and HRR enhanced*
(Parsazadeh and Duan 2017) [64]	Water	CuO nano particles*	Melting and solidification characteristics	Overall heat transfer rate improved and melting time reduced*
(Zhang <i>et al.</i> 2014) [67]	$NaNO_3/KNO_3$	Metallic foam and metallic sponge*	K	Improved*
(Gao <i>et al.</i> 2017) [68]	Erythritol	Expanded Graphite* (EG)	Thermal characteristic and thermal response	K improved by 2.5 times, latent heat reduced by 2.59% and melting time reduced by 16.7%
(Khodadadi and Hosseinzadeh 2007) [56]	Water	Copper Nanoparticles*	Thermal characteristic	K and HRR Improved*
(Xiang and Drzal 2011) [71]	Paraffin wax	EG nanoplatelets (xGnP-1 and xGnP-15) *	Thermal characteristic	Improved*
(Alkan 2006) [72]	Docosane and hexacosane	Sulfuric acid*	Thermal characteristic	Improved*
(Xu <i>et al.</i> 2016) [44]	D-Mannitol	EG*	TSD	Improved*
(Rao <i>et al.</i> 2012) [52]	n-Nonadecane	Water*	TSD	Enhanced TES capacity due to reduced mobility*
(Mettawee and Assassa 2007) [69]	Paraffin wax	Aluminum powder*	Charging and discharging processes	Charging time reduced by 60%

* Specific values not mentioned in referred literature.

portion to bottom portion [79]. A TES of another kind is developed where the heat transfer fluid is loose solid material which is disposed to inside waterproof barrier [80], in order to enhance the performance of TES heat injection system and heat recovery system is introduced, the storage material is filled in the tank and coupled with heat recovery system under lowered pressure condition [81].

A TES system containing gas inlet, gas outlet and two TES units coupled in series, each unit contains a chamber

having gas inlet, gas outlet and gas permeable TES media inclined in-between, the system also consists a flow controller connected to bypass passageways and allows the flow path of a gas through the system to transfer the thermal energy to or from the storage media. In TES storage unit having gas inlet, gas outlet and number of consecutive, downstream, gas permeable TES layers are inclined. Each layer consists of gas permeable TES media, the storage unit transfers thermal energy to or from the TES media. The inlet gas flow path is regulated by a control system, where heat transfer

takes place in downstream so that, the heat transfer will be minimal [82].

To increase the effectiveness of heat transfer to and from TES medium, highly thermal conductive elements are introduced in a self-supporting structure. The effective thermal storability of the matrix is higher than the thermal conductivity of the TES medium and suggested that, other elements with higher thermal conductivity may be used for further enhancement. A TES device consisting of a vessel housing, storage media, an input, output portion and number of heat transfer elements linked to the input and/or output. The input receives heat energy from heat source and received heat energy is transferred by heat transfer elements to the output and/or TES media [83].

A composite material of polyhydric alcohols, which provided reversible heat storage through crystalline phase transformations. These PCMs does not melt upon heating and it will be in contact with group of metals and carbon fibers are mixed in molten state, after solidification process the additives are uniformly dispersed in the solid composite. Nanoparticles (copper nanoparticles) are introduced into the PCM (paraffin wax) and resulting composite phase change material shown enhanced thermal conductivity with reference to the base PCM [84].

A TES system containing a container and a heat exchanger inclined inside the container. The heat exchanger consists a tank, a manifold and a PCM filler inside and remain in thermal contact with the TES tank [85]. A high-temperature direct-contact TES unit is designed for storing and recovering of heat energy available in range of 220 to 1100°C. A composite latent/sensible heat thermal energy storage media is used to store the energy without any heat exchangers. Solar and industrial waste heat energy can be utilized effectively through this equipment. The recovered heat can be used to operate combustion air preheating, drying and space. A thermal storing and recovering device have been developed by using PCM for latent heat storage and sensible heat is obtained from external source. The above-mentioned materials are duly stored into the tank with two compartments for two different temperatures heating portion is aligned to top surface of the tank and a cold zone is maintained at lower portion of the tank and at the middle region sensible heat storage material is filled [86].

The TES consisting of a base and fluid flow plates which creates a cavity and PCM filled into it. an extendable confined within the PCM and end plates acts like fluid flow channels. A heat transfer fluid is passed through this cavity and heat is supplied to make it charge by melting the PCM. For discharging process PCM turns from supercooled liquid state to solid state by releasing heat [87]. A TES device containing a heat receiver unit which is connected to the external heat source and expanding fluid is stored into the receiver. The heat expanding heat transfer fluid receives heat directly from source and release to the PCM through which melting occurs. Whenever heat is required same fluid can be used as

heat rejecting media for transporting the heat and makes PCM to form solid [88]. An array of electrochemical cell unit is designed and a PCM is maintained in contact with the electrochemical cell units. Another PCM is maintained in contact with the first PCM. A heat transfer occurs between the first PCM and second PCM according to the heat energy availability. First PCM receives the heat and second PCM loses the and acts like input and outputs respectively [89].

CONCLUSION

This review paper presents an in-sight study on the available thermal energy storage technology with composite Phase Change Materials (CPCM). It is seen that the thermo-physical properties enhancement is studied by characterization of CPCM by selecting different base PCMs and some novel additives. The Differential Scanning Calorimeter (DSC), Thermogravimetric Analysis (TGA), X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) are used to study the thermal properties and topography (the study of shape and features) of the CPCM. The numerical models with different material compositions are investigated at different operating conditions and compared with experimental results. Recent patents on thermal storage systems have also promoted the TES technology. The following conclusions can be drawn:

- There is a need of improvement in thermo-physical properties of traditional PCMs
- Composite phase change materials having greater potential for TES applications
- Carbon-based nanoparticles like Graphene, graphene oxide, carbon nanotubes, fullerene, graphite, graphite oxide, extracted graphite etc., are greatly enhancing the thermo-physical properties of CPCMs.
- Combination of paraffin-based PCM's and carbon-based nanoparticles can be used in CPCMs for the future TES applications.

CURRENT & FUTURE DEVELOPMENTS

Continuous advancements in thermal energy storage systems persuade us that thermal energy storage using composite Phase Change Materials (CPCM) is an attractive alternative for TES systems. In logical terms, it is only possible when CPCMs are applied to real-time applications. Large-scale development of TES systems is obligatory to completely eliminate the mis-match between source and requirement of thermal storage systems.

CONSENT FOR PUBLICATION

Not applicable.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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